

# Biodiesel Synthesis from Rubber Seed Oil via Esterification using H-Zeolit and ZrO<sub>2</sub>/ZAK Catalysts

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**Abstract:** Rubber seed oil is a non-edible oil that is very potential as a biodiesel feedstock. The synthesis of biodiesel from rubber seed oil was done by reaction of esterification free fatty acid (FFAs) and transesterification of Triglycerides (TGs) in a single step, which used heterogeneous catalysts. Zeolite is one type of catalyst that has been developed for this process. In this study the catalyst was prepared using Indonesian natural zeolite (ZAK). To increase catalytic activity, zeolite catalyst was loaded with zirconium (Zr) by wet impregnation method, followed by the process of calcination and oxidation at a temperature of 400°C for 1 hours with gas flow of O<sub>2</sub> and N<sub>2</sub>. ZAK and ZrO<sub>2</sub>/ZAK catalysts were characterized by XRD and SEM-EDS. The catalyst produced has good crystallinity as seen from sharp peaks with high intensity and high levels of Si. The catalyst activity test was done in the process of converting rubber seed oil into biodiesel. The reaction process was carried out at a temperature of 100°C with a variety of catalyst concentrations: oil: 2, 1: 4, and 1: 6 and the reaction time varied by 30, 60, and 90 minutes. The most optimum process of biodiesel produced at the ratio of catalyst 1 : 2 with reaction time of 30 minutes showed the biodiesel yield of 67,95%. Biodiesel products were tested for water content, FFA, and density of each is 0,09%, 2,15%, dan 0,89 g/cm<sup>3</sup>. GC analysis shows that the main composition of biodiesel consists of diesel fraction (C<sub>16</sub>-C<sub>20</sub>) with the most components being methyl linoleic 38,82% and methyl oleat 22,33%.

## 1 INTRODUCTION

Biodiesel is a renewable alternative fuel produced from vegetable oils or animal fats. Vegetable and animal oils are alternative energy sources that are new, renewable and environmentally friendly in addition to the fuels produced are also biodegradable and almost contain no sulfur and are environmentally friendly (Jaya et al., 2011).

Vegetable oils developed in Indonesia are sourced from palm oil, and jatropha oil, the current research has reached the utilization of palm oil and castor oil to substitute diesel fuel, but these materials have limitations, palm oil is edible oils with high selling value. According to Fukuda et al. (2001) and Tyson (2004), edible oils as biodiesel feedstock affect 60% -70% of biodiesel prices. Therefore, it is open to find alternative energy sources from vegetable oils with non-edible oil with abundant availability and lower prices.

One source of vegetable oil that can be developed is oil from rubber seeds. So far rubber seeds have not been widely used and disposed of as plantation waste. Meanwhile rubber seeds contain about 40-50% of vegetable oil which is very potential to be developed as raw material for biodiesel synthesis (Setyawardhani et al, 2010). The synthesis of biodiesel from rubber seed oil can be done by an esterification reaction, where fatty acids in rubber seeds will be reacted with short chain alcohols resulting in fatty acid methyl esters. This reaction is slow, so a catalyst is needed to reduce activation energy and accelerate the reaction. This reaction generally uses alkaline catalysts NaOH and KOH.

However, rubber seed oil has a high content of Free Fatty Acid (> 5%), the uses of alkaline catalysts can cause saponification side reactions which can reduce the rate of formation of biodiesel products. Because it is currently being developed for this process by using heterogeneous catalysts.

The advantages of heterogeneous acid catalysts are because they are less corrosive, do not need expensive separation processes, and can reduce the impact of environmental pollution (Leung et al., 2009). One type of heterogeneous acidic material is zeolite. The ability of zeolite as a catalyst is related to the availability of active centers of Bronsted acid sites and Lewis acid sites found in the channels between zeolite (Sihombing et al., 2018; Sriningsih et al., 2014; Pulungan, 2010). Modification of zeolite has been carried out by impregnating metals in carrier materials with the aim of prolonging the life of the catalyst, having good thermal stability and large surface area.

According to Sriatun and Suhartana (2002) the metal which is applied to zeolite solids through impregnation will make the metal in the zeolite as a bifunctional catalyst. Heterogeneous catalysts that are currently being developed for the production of biodiesel are zeolite which is combined with metal oxides such as ZrO<sub>2</sub>, SnO<sub>2</sub>. In addition, PbO and ZnO metal oxides were also developed as catalysts that are applied to zeolite. Singh et al., 2014 reported that PbO / zeolite showed better activity than ZnO/zeolite catalyst in the process of converting sunflower oil with high free fatty acid content (> 10%). Meanwhile, Sukmawati (2016) has made biodiesel from used cooking oil using sulfated zirconia zeolite catalyst through a transesterification reaction. From the results of this study, the conversion of triglycerides was 71.63% at the optimum condition of the reaction time for 120 minutes.

Therefore, in this study biodiesel synthesis from rubber seed oil was carried out using active natural zeolite catalyst which was treated with metal Zirconium oxide (ZrO<sub>2</sub> / ZAK). The uses of ZrO<sub>2</sub> / ZAK catalysts are expected to increase biodiesel products and produce a cheaper and environmentally friendly conversion process. In this study will be studied the effect of catalyst concentration and reaction time to obtain optimum catalyst activity.

## 2 MATERIALS AND METHOD

### 2.1 Tools

The tools used were a set of glass tools, reflux tools, sokhlet tools, analytic balance, rotary evaporator, buchner funnel, hotplate, thermometer, furnace, magnetic stirrer, 100 mesh filter, porcelain cup, oven, XRD, SEM-EDS, and GC.

The materials used were aquades, aquabides, rubber seeds oil, commercial natural zeolites (Bratachem), HCl (Merck pa), ZrCl<sub>4</sub> (Merck pa), nitrogen gas, NaOH (Merck pa), H<sub>2</sub>SO<sub>4</sub> (Merck pa), PP indicators, AgNO<sub>3</sub> (Merck pa), H<sub>3</sub>PO<sub>4</sub> (Merck pa), n-Hexane (technical), and CH<sub>3</sub>OH (Merck pa).

### 2.2 Preparation of Rubber Seed Oil

The rubber seeds were separated from the shell, then the rubber seeds dried under the sun for 2-3 days after that mashed using a blender. The refined rubber seeds then extracted to obtain the oil with n-hexane solvents at 60°C for 2 hours (5 cycles) continued with separated the solvent using a rotary evaporator to produce pure rubber seed oil, then analyzed to determine the levels of free fatty acids (FFA), density and water content.

### 2.3 Preparation of Natural Zeolite

Natural zeolite was smoothed and filtered with a 100 mesh filter. Then washed with distilled water for 24 hours at room temperature. Zeolite filtered and the precipitate dried at 100°C. The natural zeolite sample was dehumidated with 3M HCl and then refluxed at 90°C for 30 minutes. The reflux solution was filtered and the resulting sediment was washed with distilled water until the pH of the washing water was neutral. The precipitate was then dried at 120°C for 3 hours, then calcined at 400°C for 1 hour with gas nitrogen flow ( $\pm$  20 mL / minute) to obtain acid-activated natural zeolite (H-Zeolite) (Sihombing et al., 2018).

### 2.4 Preparation of ZrO<sub>2</sub>/ZAK Catalyst

An amount of 1% ZrCl<sub>4</sub> (% w Zr) was dissolved with aquabides in a round bottom flask and then added to ZAK, the mixture stirred for 3 hours at 80°C after that zeolite was dried. Zeolite was then oxidized with O<sub>2</sub> gas at 400°C for 1 hour. The ZrO<sub>2</sub> / ZAK catalyst produced was characterized by FTIR spectrometers Shimadzu type 8201-FC, X-ray diffractometer Shimadzu 6100 using Cu K $\alpha$  radiation at 40 Kv and 30 mA with scanning rate of 2 $\theta$  min<sup>-1</sup> in range 2 $\theta$  7° – 70°, SEM and SEM-EDS used Zeis type EPOMH 10 Zss.

### 2.5 Synthesis of Biodiesel

Biodiesel made by mixing 99% methanol and zeolite as a catalyst in a base flask with a ratio of zeolite: oil that is 1: 2, 1: 4, and 1: 6 (v/v). The mixture then

added to rubber seed oil with a ratio of oil: methanol 1: 6 (v/v) and stirred at a speed of 600 rpm for 30, 60, and 90 minutes at 65°C at a pressure of 1 atm. The mixture continued by filtered with a Buchner funnel. Then decanted for 2 days. The biodiesel produced was analyzed for FFA content, water content, density, and GC characterization.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization of Natural Zeolites

FTIR analysis was used to determine the functional groups of zeolite samples. Based on the ZAK spectra in figure 1 it can be seen that the TO<sub>4</sub> group absorption characteristic of zeolite observed at 1089.98 cm<sup>-1</sup>. The absorption band of Si-O / Al-O group at 723.92 cm<sup>-1</sup> and 794.95 cm<sup>-1</sup>. Hamdan (1999) reported that in the 900-1250 cm<sup>-1</sup> band was an asymmetrical range of the TO<sub>4</sub> group, internal Si-O / Al-O (TO) bending appeared in the 420-500 cm<sup>-1</sup> region while for the external would appear at 700-780 cm<sup>-1</sup> (Hamdan, 1992). Sihombing et al (2018) reported that asymmetrical range vibrations of the TO<sub>4</sub> zeolite group were in the range of 1000-1100 cm<sup>-1</sup>. Asymmetric vibration absorption of the TO<sub>4</sub> group from Sarulla zeolite was at 1042.16 cm<sup>-1</sup> (Nasution et al., 2019).

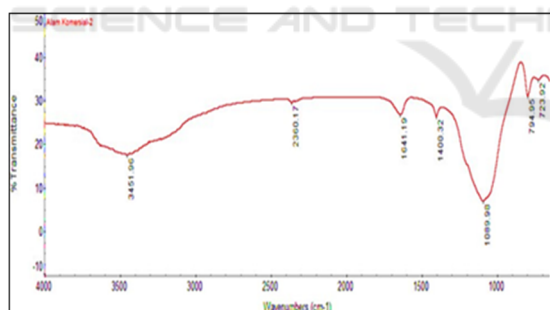


Figure 1: FTIR spectrum of commercial natural zeolite

Measurements with X-ray diffraction were carried out to identify the crystallinity of the initial natural zeolite, natural zeolite after acid activation and after ZrO<sub>2</sub> was introduced. The results of XRD analysis of each sample are presented in Figure 2. Sharp peaks with high intensity show good crystallinity. Figure 2 shows that the treatment of HCl 3M (H-zeolite) activation provides an increase in intensity on some of the main zeolite peaks at 20-30 2 theta degrees. This is due to the loss of amorphous and crystalline impurities that cover the zeolite pores (Waluto et al., 2017; Sihombing et al.,

2018). In this figure ZrO<sub>2</sub>/ZAK also shows the increasing intensity of the main zeolite peak. This shows that the impregnation of ZrO<sub>2</sub> metal is distributed evenly on the surface and pore of zeolite. While the oxidation process at a high temperature of 500°C results in the loss of organic and inorganic impurities in zeolite pores.

Based on table 1 Typical peaks of zeolite are seen in H-Zeolite and ZrO<sub>2</sub>/ZAK at position 2 theta degrees which are almost the same although with slightly different intensities. This shows that acid treatment is dealumination with 3M HCl in H-Zeolite and thermal treatment ie oxidation on ZrO<sub>2</sub> / ZAK does not damage the structure of zeolite even though there is a decrease in peak intensity of ZrO<sub>2</sub>/ZAK. The decrease in peak intensity in metal-borne natural zeolites proves that metals have been on the surface of natural zeolites (Rianto et al., 2012).

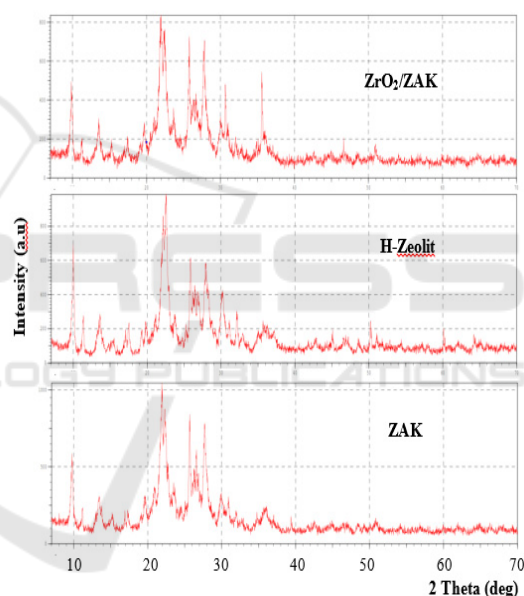


Figure 2: Diffraction pattern comparison of ZAK, H-Zeolite and ZrO<sub>2</sub>/ZAK

Table 1: The main peak intensity of ZAK, H-Zeolite and ZrO<sub>2</sub>/ZAK

Catalyst	2θ (°)	Intensity (counts)
ZAK	9.87	364.90
	22.54	548.03
	35.74	142.15
H-Zeolite	10.04	304.2
	21.99	623.52
	35.87	142.01
ZrO <sub>2</sub> /ZAK	9.03	302.21
	27.7	527.17
	35.53	256.24

The SEM data showed information on surface topology and metal dispersion that is applied to zeolite, while from EDS data of chemical composition is obtained on the surface of the sample. Figure 3a and 3b describe surface topologies of H-zeolite and ZrO<sub>2</sub> / ZAK with a magnification of 1000 times. In figure 3a the surface micrograph of H-zeolite shows a surface structure consisting of lamellar with a small size that is uneven and there are still lumps. While ZrO<sub>2</sub> / ZAK in figure 3b shows a smooth and more homogeneous surface structure. This data supports XRD data which shows the metal dispersing process does not occur sintering. Metal oxides are distributed evenly in zeolite pores.

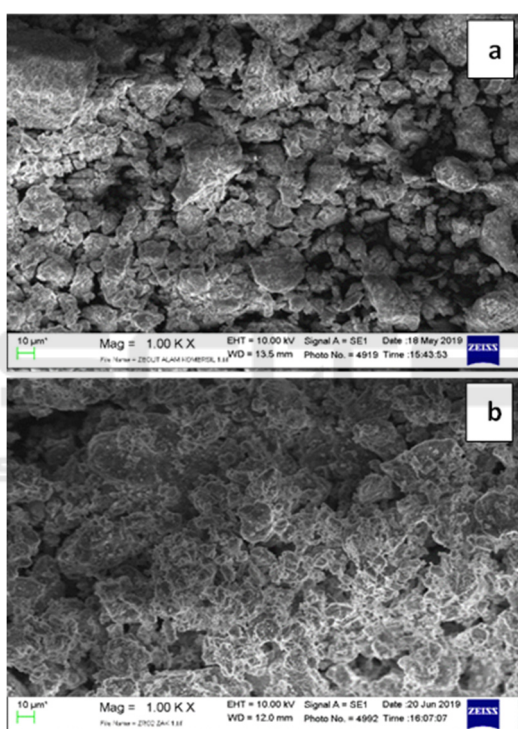


Figure 3: Surface topology enlarged 1000×. (a) natural zeolite, (b) ZrO<sub>2</sub>/ZAK

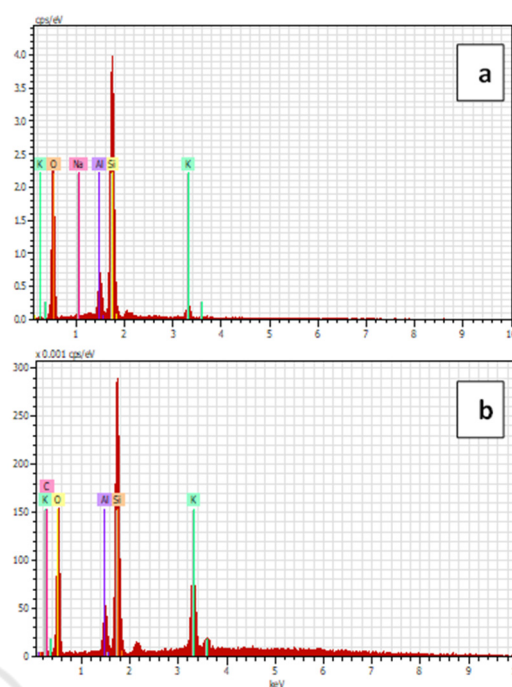


Figure 4: Graph of chemical composition in (a) H-Zeolite, (b) ZrO<sub>2</sub>/ZAK

### 3.2 Synthesis of Biodiesel from Rubber Seed Oil

Rubber seed oil is obtained by soxhlet extraction method using technical n-hexane solvents. The yield of rubber seed oil obtained was 43.79%. Characteristics of rubber seed oil based on practice and standards are presented in table 2. Rubber seed oil is obtained by soxhlet extraction method using technical n-hexane solvents. The yield of rubber seed oil obtained was 43.79%. Characteristics of rubber seed oil based on practice and standards are presented in Table 2.

Table 2: Characteristics of rubber seed oil (RSO) and biodiesel

Characteristics	ASTM D6751 (biodiesel)	RSO	Bio Diesel
Water content (%)	0.05	1.101	0.09
FFA (%)	< 2	10.401	2.15
Density (g/cm <sup>3</sup> )	0.860-0.900	0.9097	0.89

The process of converting rubber seed oil with ZAK and ZrO<sub>2</sub> / ZAK catalysts is carried out by a one-step process. In this reaction, esterification of free fatty acids and transesterification of



triglycerides occur the same process. The results of the conversion of biodiesel products obtained are presented in table 2. The optimum process conditions were obtained at a catalyst ratio: 1: 2 and a temperature of 30°C with a 67.95% biodiesel yield value. To see the effect of variations in the catalyst ratio: oil and process temperature, data made in graphical form as shown in Figures 5 and 6. The ratio of the catalyst: oil and reaction time affects the conversion value of the biodiesel.

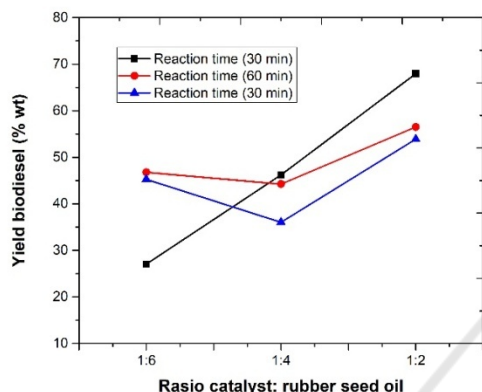


Figure 5: Graph of the relationship of reaction time to biodiesel yield

In Figure 5, it can be seen that the most optimum of reaction time which produces the highest yield is 30 minutes. In general, the longer the esterification reaction time, the greater the conversion of oil to biodiesel because of the greater the chance of collisions between molecules occur. But at the reaction time for 60 minutes and 90 minutes there was a decrease in the yield of biodiesel produced, this is because the reaction temperature used is close to the boiling point of methanol (65°C) causing some of the methanol to evaporate as the reaction time increases. This resulted in a reduced molar ratio of methanol to esterification oil. Tiamina et al. (2019) reported that evaporation of methanol resulted in a reduced molar ratio of methanol to biodiesel production so that the yield of biodiesel produced decreased.

Figure 6 shows that biodiesel yield increases with increasing of catalyst:oil ratio. The increasing of the concentration of the catalyst will reduce the activation energy for the esterification reaction thereby increasing the number of molecules activated and reacting to form the fatty acid methyl ester. At a reaction time of 30 minutes, a larger catalyst: oil ratio shows a sharp increase in the conversion of biodiesel products. Different trends are shown at reaction times 60 and 90 minutes, where the catalyst ratio increases: oil shows a

decrease in the conversion of biodiesel products and shows an increase in a larger ratio. It can be understood that at ratio: catalyst 1: 2 it is possible to meet the active side of the catalyst with reactants greater compared with the ratio of 1: 6. So that the chance for contact between the reactants and the catalyst to be greater so that it will produce a catalyzed reaction that is also getting bigger. This is indicated by the increasing conversion of biodiesel products produced.

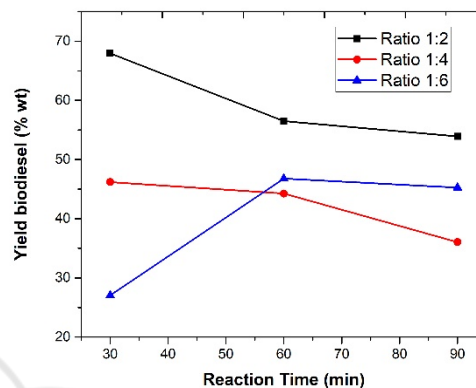


Figure 6: Graph of the relationship of ratio of rubber seed oil to zeolite with the biodiesel yield

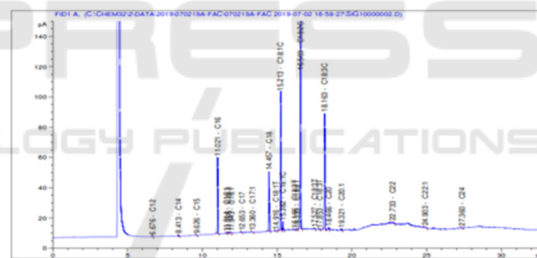


Figure 7: GC chromatogram of biodiesel product at optimum condition.

Table 3: Chemical component of biodiesel

No.	Component	Methyl ester	Composition (%)
1.	C16	Methylpalmitate	9.80
2.	C18	Methylstearate	8.85
3.	C18 : 1	Methyloleate	22.33
4.	C18 : 2	Methylinoic	38.82
5.	C18 : 3	Methylinolenic	18.22
6.	C20	Methylarachidat	0.33

Figure 6 shows the chromatogram of biodiesel products obtained at optimum conditions, with the main content are methyl linoleic and methyl oleate with a percentage of 38.82% and 22.33% respectively.

## 4 CONCLUSION

The acid activation process increases zeolite crystallinity. The impregnated of zirconium oxide (ZrO<sub>2</sub>) causes a shift and decreases the ripple intensity of zeolite, but does not damage the zeolite crystal structure. In the process of converting biodiesel from rubber seed oil the optimum yield was 67.95% at a catalyst ratio of 1: 2 with a reaction time of 30 minutes. The main composition of biodiesel consists of C16-C20 diesel fraction with the most components, namely methyl linoleic (C18: 2) as much as 38.82% and methyl oleate (C18: 1) as much as 22.33%.

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